ON THE LENGTH OF MOLECULAR THREADS

PHYSICS

1966

SovietRxiv

Abstract

Full Text

UDC 621.380

PHYSICS

Academician of the Academy of Sciences of the Ukrainian SSR A. P. KOMAR

ON THE LENGTH OF MOLECULAR THREADS

AT THE TIP OF AN ELECTRON PROJECTOR,

WHICH GIVE RISE TO "MOLECULAR" PATTERNS

It may be considered established that the appearance of "molecular" patterns discovered by Müller (1) is connected with the microrelief of a nonuniform adsorbate layer of substances with delocalized electron bonds on the cold tip of a projector.

According to (2,3), the electron emission of an adsorbate of the indicated substances may be interpreted as the emission of a layer on which molecular threads oriented in the electric field protrude, transmitting electron waves from the metal of the substrate in the same way as hollow metallic or solid dielectric waveguides transmit electromagnetic waves. In (2) the transverse dimensions of these threads were determined; they proved to be of the order of 10^{-8} cm (more precisely $8.5 \cdot 10^{-8}$ cm). The longitudinal dimensions of the molecular threads have not yet been determined.

In accordance with the experimental data (2), it may be assumed that the field-electron emission of an adsorbate—organic molecular substances with double bonds, such, for example, as phthalocyanines—is similar to that of metals. This means that the electric field does not penetrate deeply into the adsorbate.

Probably this assertion is not valid for weak fields and substances in which the concentration of current carriers is smaller than in phthalocyanines. We adopt it in order to facilitate the solution of the problem posed.

If a cylindrical metallic or metal-like thread of radius ρ is in an electric field, then per unit area of the hemispherical end of the thread there acts a ponderomotive force

$$p = E^2/8\pi(300)^2, \tag{1}$$

where E is the electric-field strength in volts per 1 cm. This force is balanced by the forces of surface tension and by elastic forces. If γ is the surface tension and σ the elastic stress in the thread, then one may write

$$E^2/8\pi(300)^2 = \gamma/\rho + \sigma. \tag{2}$$

If in what follows we restrict ourselves to cases of adsorption of organic molecular substances, then γ will not exceed 100 dyn/cm. For a radius of 10^{-7} cm, $\gamma/\rho \leq 10^9$ dyn/cm^2. The second term, if the experimental data (^{4}) are used, is at least an order of magnitude larger. It is clear that in approximate calculations the first term γ/ρ may be neglected. If the cross-sectional area of the thread S is the same along its entire length, then the rupture stress σ_{rupt} may be related to the electric-field strength producing rupture E_{rupt} by means of the relation

$$E^2_{\text{rupt}} = 8\pi(300)^2\sigma_{\text{rupt}} \quad \text{or} \quad E_{\text{rupt}} \simeq 1.5 \cdot 10^3\sqrt{\sigma_{\text{rupt}}}. \tag{3}$$

Using the maximum experimental value $\sigma_{\text{rupt}} = 360$ kg/mm^2 $= 3.53 \cdot 10^{10}$ dyn/cm^2, determined in (^{5}) for polymerized polyoxymethylene, and assuming that for phthalocyanine threads···

close values of σ_{break} will be obtained; we obtain the estimate

$$E'_{\text{break}} = 2.82 \cdot 10^8 \text{ V/cm}.$$

This value of E_{break} differs little from the value $E = 2.1 \cdot 10^8$ V/cm, which destroys molecular patterns, according to the work$^{(6)}$.

For the case of a cylindrical conducting thread of radius ρ, it is easy to establish the relation between the length of the thread and the field strength E'_ρ at the hemispherical end of the thread. Let us first consider the potential of a free sphere of radius ρ (hereafter, a sphere ρ), located at a distance $d = R + l - \rho = R + x$ from the charge of a hemispherical tip of radius R (see Fig. 1). This charge may be regarded as a point charge, concentrated at the center of the sphere R and equal to

$$q = V_R/R, \tag{4}$$

where V_R is the potential of the tip relative to ground. According to $^{(7)}$, the potential V of a conducting sphere of radius $\rho \ll R$, located in the field of a point charge q at a distance d from it, is determined by the expression

$$V = \frac{q}{d}\sum_{n=0}^{\infty}\left(\frac{r}{d}\right)^n P_n(\cos\theta), \tag{5}$$

Fig. 1

Figure 1: Fig. 1

where r is the distance from the origin of coordinates, situated at the center of the sphere ρ, and $P_n(\cos\theta)$ is a Legendre polynomial. If $r/d \ll 1$, then it is possible to restrict ourselves to two terms of the sum; therefore, at $r = \rho$,

$$V = q/d + q\rho/d^2. \tag{6}$$

Fig. 1

If the free sphere ρ is connected by an infinitely thin conducting thread to the tip, then the potential of this sphere becomes equal to the potential of the tip. For equalization it is necessary to add to the potential of the sphere ρ some quantity ΔV; we obtain

$$V + \Delta V = V_R. \tag{7}$$

The increment ΔV can arise only as a result of supplying a charge q' to the sphere ρ. Substituting into (7) the expressions for V, ΔV, and V_R through the charges, and taking into account that $(d-R)/d = x/(R+x)$, we obtain

$$q' = \frac{x}{R+x} V_R \rho. \tag{8}$$

Knowing q', one can calculate the theoretical field strength at the surface of the sphere E'_ρ:

$$E'_\rho = \frac{q}{d^2} + \frac{q'}{\rho^2} \simeq \frac{q'}{\rho^2} = \frac{x}{R+x}\frac{V_R}{\rho}. \tag{9}$$

The real field strength E'_ρ, if one takes into account that the sphere is not free, will be k times smaller. The same value of k may be adopted as in the case of metallic whiskers. According to (8), k may be taken equal to 5.

An estimate of the maximum value of l, or $x = l - \rho$, can be obtained if one sets $E_{\text{break}} = E_\rho$. Using (9) and (3), we obtain

$$x = \frac{1.5 \cdot 10^3 \sqrt{\sigma_{\text{break}} R \rho k}}{V_R}. \tag{10}$$

Substituting into formula (10) the numerical values $R = 10^{-5}$ cm, $\rho = 10^{-7}$ cm, $k = 5$, $V_R = 5 \cdot 10^3$ V, $\sigma_{\text{break}} = 3.53 \cdot 10^{10}$ dyn/cm^2, we obtain the estimate $x = 2.82 \cdot 10^{-7}$ cm.

If one uses the theoretical estimate of the strength of the thread, assuming that it is due to a single C—C bond, equal to $3.2 \cdot 10^{11}$ dyn/cm^2 (9), then, of course, the value of x will be larger: $x = 8.5 \cdot 10^{-7}$ cm. Incidentally, the value of E_{break} for the theoretical estimate of the strength due to the C—C bond should not exceed the value E_{desorb} of the electric field that desorbs carbon atoms, given in (10):

$$E_{\text{break}} = 8.5 \cdot 10^8 \text{ V/cm} < E_{\text{desorb}} = 1.43 \cdot 10^9 \text{ V/cm}.$$

An estimate of the values of E_ρ on the basis of data on the autoelectron emission of threads producing "molecular" spots can be made under the assumption that the work function φ is independent of E, and provided there is a known dependence of the emission-current density j on E and φ. For metals, the current density j is related to E and φ by the Fowler—Nordheim formula (11). There exist qualitatively analogous formulas for semiconductors as well, but they are more complicated and have not been tabulated; therefore the indicated formula is preferable for approximate calculations. Using Dolan' s tables, given in (11), one can, knowing the work function and the electron-current density forming the "molecular" spots, determine E_ρ. This operation cannot be carried out flawlessly, since the exact values of the work function for phthalocyanines are unknown. If, according to (12), one takes $\varphi = 7$ eV for phthalocyanine and the emission-current density $j = 10^5$ A/cm, then, according to Dolan' s tables, E_ρ will be of the order of 10^8 V/cm. The order of magnitude of the values of E_ρ thus turns out to be the same as that calculated from the strength of the threads and from the data of (6).

The agreement in the order of the estimates and in the order of the experimental values of E_ρ and x cannot be accidental, and therefore it may be asserted that the values of x have physicochemical meaning and do not contradict the wave theory (13) of "molecular" patterns.

Physical-Technical Institute named after A. F. Ioffe
Academy of Sciences of the USSR

Received
18 IX 1965

REFERENCES

[1] E. W. Müller, *Zs. Naturforsch.*, **5a**, 473 (1950).
[2] A. P. Komar, V. P. Savchenko, DAN, **159**, 1310 (1964).
[3] A. P. Komar, V. P. Savchenko, *Fiz. tverd. tela*, **7**, 759 (1965).
[4] E. M. Naporovskii, Yu. A. Ospin et al., UFN, **67**, 625 (1959).
[5] A. I. Slutsker, A. E. Gromov, V. S. Pshezhetskii, *Fiz. tverd. tela*, **6**, 456 (1964).
[6] A. I. Melmed, E. W. Müller, *J. Chem. Phys.*, **29**, 1037 (1958).
[7] J. A. Stratton, *Electromagnetic Theory*, N. Y., 1941, p. 201; J. A. Stratton,

Theory of Electromagnetism, 1948, p. 183.
[8] R. Gomer, *J. Chem. Phys.*, **28**, 457 (1958).
[9] P. P. Kobeko, *Amorphous Substances*, Publishing House of the USSR Academy of Sciences, 1952, p. 217.
[10] E. V. Müller, UFN, **77**, 482 (1962).
[11] M. I. Elinson, G. F. Vasil' ev, *Autoelectron Emission*, M., 1958, p. 43.
[12] R. Gomer, D. A. Speer, *J. Chem. Phys.*, **21**, 73 (1953).
[13] A. P. Komar, A. A. Komar, ZhTF, **31**, 231 (1961); **32**, 867 (1962).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.